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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Continuous Preparation of Aqueous Secondary Polyacrylate Dispersions

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Abstract of the Disclosure: Aqueous secondary polyacrylate dispersions having a long shelf life and based on the polyacrylate resin systems are prepared by means of intensively dispersing screw extruders by a continuous process, on which the preparation of the secondary dispersion is carried out, after neutralization of the solvent-free copolymer melt or of the dissolved copolymer, in the shearing section of the screw extruder, and

the specific energy input is 0.001-0.25 kWh/kg, the residence time in the shear field is 0.1-120 sec and the shear gradient is 1,000-12,000 1/sec.

Continuous preparation of aqueous secondary
polyacrylate dispersions

5 The present invention relates to a continuous process for the preparation of aqueous secondary polyacrylate dispersions having a long shelf life and based on polyacrylate resin systems by means of intensively dispersing screw extruders.

10 Preferably used resins are self-emulsifying polyacrylates. The systems are self-emulsifying owing to the content of hydrophilic groups. These hydrophilic groups are preferably acid groups which, after neutralization and salt formation, render the polymer emulsifiable in water. The polyacrylates are prepared by free radical solution copolymerization of (meth)acrylates and possibly
15 vinylaromatics. Particularly preferred monomers are acrylic acid, n-butyl acrylate, methyl methacrylate, hydroxyethyl methacrylate and styrene. The self-emulsifying resins to be dispersed may be copolymers containing acrylic acid, which are described in, for example, German Published Application DAS 2,507,842. Mixtures of two copolymers, only one of which contains
20 monomers carrying acid groups as a comonomer building block, are particularly preferred. After the neutralization step, these acid groups are of decisive importance for the dispersibility of the copolymer mixture. These
25 systems are described in European Patent 225,612.

The acid number of typical copolymer mixtures is from 12 to 35. The molecular weights (MW) are typically of the order of from 70,000 to 100,000. The copolymers
30 are obtained in organic solvents by free radical polymerization. The preferred solvent is isobutanol. The solids contents of the solution polymers are typically from 70 to 85% by weight. The viscosities of the solvent-containing systems are of the order of 40 Pa.s at 90°C. The melt viscosities of the solvent-free
35 polymers are from 100 to 10,000 Pa.s at 120°C. The neutralizing agent used is preferably aqueous ammonia.

The ammonia concentration may be preferably from 5 to 25% by weight. In addition to ammonia, organic amines, for example triethylamine, dimethylethanolamine, etc., are also suitable.

5 The dispersion is stabilized by the carboxylate groups which are present at the surface of the latex particles. Such secondary dispersions are free of emulsifiers or protective colloids. Film properties can therefore be achieved with these systems, for example
10 high water resistance, which cannot be realized with emulsion polymers (primary dispersions).

According to the prior art, aqueous secondary polyacrylate dispersions are prepared from copolymer solutions by the following process steps:

- 15 1) Neutralization of acidic or basic groups with bases or acids
 2) Dispersion of the dissolved polymer in water
 3) Removal of the organic solvent by distillation.

Usually, these process steps are carried out in
20 stirred kettles and are likewise described in European Patent 225,612. The removal of the organic solvent by distillation can be effected in the stirred kettle only after the polymer has been dispersed, since the viscosity of the polymers without the solvent would be too high to
25 enable them to be dispersed in a stirred kettle. A disadvantage of this procedure is that water is evaporated off with the organic solvent and the energy costs are thus increased. Consequently, the cycle time for the preparation of the dispersion also increase.
30 However, the most serious disadvantage of this process is the expensive distillation step for separating off the water from the organic solvent, which is necessary when working up the distillate.

According to German Laid-Open Application DOS
35 3,911,945, the organic solvent can be separated from the polymer resin before the dispersing process in the stirred kettle in the case of certain contact adhesive

secondary dispersions. These polymer resins have a low molecular weight and a low glass transition temperature. Owing to the high viscosity of the novel polyacrylate resins, this procedure is not possible.

5 European Patent 384,165 describes a continuous process for the preparation of aqueous, non-self-emulsifying polymer dispersions from highly viscous reaction resins. However, surfactants or protective
10 colloids must be added in the preparation of this dispersion since these systems are not self-emulsifying. Neutralization of functional groups is therefore dispensed with.

 In contrast to the process described in European Patent 384,165, self-emulsifying systems are used in the
15 novel process.

 The neutralization of the acidic or basic groups before the dispersing step with water is of decisive importance for the preparation of a novel secondary polyacrylate dispersion.

20 The neutralized carboxylate groups lead to a stable, on-spec dispersion in the dispersing step. The preparation of an on-spec dispersion by means of a high and intensive energy output is not possible without prior neutralization.

25 In contrast to European Patent 384,165, the addition of surfactants or protective colloids is not necessary for the novel secondary polyacrylate dispersions.

 DE 38 30 535 describes the continuous preparation
30 of aqueous synthetic wax dispersions. In the novel process, the neutralization of the solvent-free copolymer melt can also be carried out in a twin-screw extruder. Surprisingly, however, all extruder types mentioned there are unsuitable for dispersing the neutralized, solvent-
35 free copolymer melt, since dispersing is not sufficiently intensive. Instead, dispersing must be carried out in the intensively mixing shearing section (rotor/stator) of

a screw extruder.

It is an object of the present invention to provide a continuous process for the preparation of aqueous secondary polyacrylate dispersions having a long shelf life.

We have found that this object is achieved, according to the invention, if the preparation of the secondary dispersions is carried out, after the neutralization of the solvent-free copolymer melt or of the dissolved copolymer, in the shearing section of a screw extruder, and

the specific energy input is 0.001-0.25 kWh/kg, the residence time in the shear field is 0.1-120 sec and the shear gradient is 1,000-12,000 1/sec.

The residence time in the shear field is preferably from 0.5 to 2 sec; the specific energy input is preferably from 0.001-0.2 kWh/kg. A specific energy input above 0.25 kWh/kg causes damage to the product, while an energy input of less than 0.001 kWh/kg leads to insufficient dispersing.

Before dispersing with water, neutralization of acidic or basic groups of the copolymer melt should be carried out.

This neutralization is carried out, according to the invention, by metering aqueous ammonia solution into the copolymer melt in a self-purging twin-screw extruder, for example a ZSK (Werner & Pfleiderer), and mixing it with the copolymer melt in a mixing zone.

The mixing zone used may advantageously comprise kneading elements, the specific energy input being 0.005 to 0.05 kWh/kg and the residence time in the mixing zone being 0.1-60 sec.

Alternatively, the neutralization can also be carried out in the shearing section of a screw extruder.

This neutralization step is of decisive importance for the preparation of stable, on-spec dispersions in the subsequent dispersing step.

The secondary dispersions prepared by this newly developed process are speck-free and have a long shelf life and an on-spec particle size distribution.

5 This leads to high-quality secondary polyacrylate dispersions.

An object of the present invention was to disperse the solvent-free copolymer melt in order to dispense with the expensive distillation process for separating water from the organic solvent.

10 This object is achieved by first distilling off the solvent from the solvent-containing copolymer solution. Some of the solvent may be removed in the stirred kettle itself after the polymerization. The further removal of the solvent is part of the prior art and can be carried out, for example, in a stopper tube degasser or in a twin-screw extruder.

15 It is advantageous to remove from the dispersion some of the ammonia, preferably used for neutralization, in a devolatilization step after the dispersing. This leads to dispersions having a substantially lower viscosity. The devolatilization step is part of the prior art and can be carried out, for example, in a Fryma vacuum deaerator, a falling film evaporator or a twin-screw extruder or in a stirred kettle having a stripping apparatus.

20 An apparatus which can advantageously be used for the process according to the present invention is shown in the process flow diagram.

25 The highly viscous copolymer solution is stored in kettle 1, and the solvent content may correspond to the solvent content required for the polymerization or may have already been reduced in a preceding stripping operation, which is sufficiently known from the prior art.

30 To ensure that the copolymer solution exhibits flow, the kettle 1 can be heated. The shut-off valve 2 is installed between kettle 1 and the gear pump 3. The

5 copolymer solution is metered in by means of the gear pump of the heatable twin-screw extruder 14, which is driven by an electric motor 10. The first section of the screw extruder 11 serves as a pressure build-up zone, while the remaining solvent is evaporated from the copolymer solution by means of reduced pressure 4 in the second screw section 12. The solvent can be collected in the cold trap 5. The valve 6 serves as an outflow valve for the cold trap 5.

10 The aqueous ammonia solution for neutralization the carboxylate groups is stored in the kettle 7. The ammonia solution having an ammonia concentration of, preferably, 5-25% by weight of ammonia can be metered into the twin-screw extruder via the reciprocating pump. 15 The screw section 13, equipped with kneading elements, serves as a mixing zone for mixing the solvent-free copolymer melt with the aqueous ammonia solution and hence for neutralizing said melt. In addition, the screw zone 13 functions as a pressure build-up zone in order to 20 meter the neutralized, solvent-free copolymer melt into the screw extruder 26.

A high-speed single-screw extruder which is driven by an electric motor 21 can be used as screw extruder 26 having a shearing section.

25 The screw extruder can be heated via a double jacket with cooling/heating media 27.

The solvent-free, neutralized copolymer melt is metered into the first section of the screw extruder 22. This screw section is equipped with conveying screws 30 which transport the copolymer melt into the dispersing zones 23 and 24. Dispersing is effected in the dispersing zones 23 and 24 by adding water. Adding water at two points is advantageous; the addition of water at only one point may lead to speck formation.

35 The demineralised water is stored in the kettles 15 and 18; the kettles are heatable in order to heat the demineralised water. The valves 16 and 19 serve as

shut-off members. The demineralised water is metered by means of reciprocating pumps 17 and 20.

5 The dispersing zones 23 and 24 must be in the form of dispersing mixing zones having a narrow shear rate distribution, in order to minimize the required dispersing time.

10 The dispersing zones 23 and 24 are designed so that a specific energy input of from 0.001 to 0.25 kWh/kg, a shear gradient of from 1,000 to 12,000 sec^{-1} and a residence time of from 0.1 to 120 sec can be set. Specific energies greater than 0.25 kWh/kg cause damage to the product, while an energy input of less than 0.001 kWh/kg leads to insufficient dispersing.

15 Rotor/stator systems having narrow gap widths can advantageously be used.

The aqueous secondary polyacrylate dispersion 28 is discharged continuously from the screw extruder by means of the conveying screws in the screw section 25.

EXAMPLE 1

20 A copolymer solution according to Example 2 of European Patent 225,612, having a solvent content of 23%, is metered into the twin-screw extruder (ZSK) by means of a gear pump.

25 A mass flow of copolymer solution of 20.9 kg/h is established.

The solvent (isobutanol) is completely evaporated off in the devolatilization barrel of the ZSK at 120°C and is collected in a cold trap.

30 Further along the ZSK, 2.1% strength aqueous ammonia solution is added by means of a reciprocating pump, in order completely to neutralize the solvent-free copolymer.

The established mass flow of the ammonia solution is 4 kg/h.

35 In the mixing zone of the ZSK, which is equipped with kneading elements, the residence time in the shear field is 21 sec and the specific energy input is

0.01 kWh/kg.

The solvent-free, neutralized copolymer is metered from the ZSK, at 80°C, into the high-speed single-screw extruder.

5 The speed is 1,000 rpm.

In the single-screw extruder, two dispersing stages with rotor/stators are used in order gradually to add demineralised water heated to 80°C.

10 The established mass flow is 8 kg/h at the first water addition pump and 8.4 kg/h at the second water addition pump.

15 The shear gradient in the rotor/stator having a gap width of 0.5 mm is $5,500 \text{ s}^{-1}$, the residence time in the shear field of the rotor/stator is 11 sec and the specific energy input is 0.03 kWh/kg.

Characteristics of the dispersion are shown in Table 1, column 1. The viscosity of the dispersion can be reduced by downstream removal of gaseous NH_3 .

EXAMPLE 2

20 A copolymer solution according to Example 2 of European Patent 225,612, having a solvent content of 23%, is metered into a twin-screw extruder (ZSK) by means of a gear pump.

25 A mass flow of copolymer solution of 20.2 kg/h is established.

The solvent (isobutanol) is completely evaporated off in the devolatilization barrel of the ZSK at 120°C and is collected in a cold trap.

30 The solvent-free copolymer is metered, at 80°C, from the ZSK into the high-speed single-screw extruder.

The speed of the single-screw extruder is 800 rpm.

35 In the single-screw extruder, three dispersing stages with rotor/stators are used in order first to carry out the neutralization step and then gradually to add demineralised water heated to 60°C.

In the first dispersing stage of the single-screw

extruder, 4.3% strength aqueous ammonia solution is added by means of a reciprocating pump in order completely to neutralize the solvent-free copolymer.

5 The established mass flow of the ammonia solution is 2.1 kg/h.

The residence time in the neutralization zone of the single-screw extruder is 24 sec.

10 In the subsequent two dispersing stages, demineralised water is gradually added. The mass flow is set at 8 kg/h at the first water addition point and 10 kg/h at the second water addition point.

15 The shear gradient in the rotor/stator having a gap width of 0.5 mm is $4,400 \text{ s}^{-1}$, the residence time in the shear field of the rotor/stator is 15 sec and the specific energy input is 0.1 kWh/kg.

The characteristics of the dispersion are shown in Table 1, column 2.

The viscosity of the dispersion can be reduced by downstream removal of gaseous NH_3 .

20

EXAMPLE 3

A copolymer solution according to Example 2 of EP-A 225,612, having a solvent content of 23%, is metered into a twin-screw extruder (ZSK) by means of a gear pump.

25 A mass flow of copolymer solution of 20.2 kg/h is established.

In the devolatilization barrel of the ZSK, the copolymer solution is concentrated to a solvent content of 12% by weight at 120°C.

30 The concentrated copolymer solution is metered, at 120°C, from the ZSK into the high-speed single-screw extruder.

The speed of the single-screw extruder is 1,000 rpm.

35 In the single-screw extruder, three dispersing stages with rotor/stators are used in order first to carry out the neutralization step and then gradually to add demineralised water heated to 60°C.

In the first dispersing stage of the single-screw extruder, 4.3% strength aqueous ammonia solution is added by means of a reciprocating pump in order completely to neutralize the solvent-free copolymer.

5 The established mass flow of the ammonia solution is 2.1 kg/h.

The residence time in the neutralization zone of the single-screw extruder is 20 sec.

10 In the subsequent two dispersing stages, demineralised water is gradually added. The mass flow is set at 8 kg/h at the first water addition point and 10 kg/h at the second water addition point.

15 The shear gradient in the rotor/stator having a gap width of 0.5 mm is $5,500 \text{ s}^{-1}$, the residence time in the shear field of the rotor/stator is 14 sec and the specific energy input is 0.06 kWh/kg.

The characteristics of the dispersion are shown in Table 1, column 3.

EXAMPLE 4

20 A copolymer solution according to Example 2 of EP-A 225,612, heated to 80°C and having a solvent content of 23%, is metered into the single-screw extruder (ZSK) by means of a gear pump.

25 The speed of the single-screw extruder is 1,000 rpm.

In the single-screw extruder, three dispersing stages having rotor/stators are used in order first to carry out the neutralization step and then gradually to add demineralised water heated to 60°C .

30 In the first dispersing stage of the single-screw extruder, 4.3% strength aqueous ammonia solution is added by means of a reciprocating pump in order completely to neutralize the copolymer solution.

35 The established mass flow of the ammonia solution is 2.1 kg/h.

The residence time in the neutralization zone of the single-screw extruder is 19 sec.

In the subsequent two dispersing stages, demineralised water is gradually added. The mass flow is set at 8 kg/h at the first water addition point and 10 kg/h at the second water addition point.

5 The shear gradient in the rotor/stator having a gap width of 0.5 mm is $5,500 \text{ s}^{-1}$, the residence time in the shear field of the rotor/stator is 13 sec and the specific energy input is 0.01 kWh/kg.

10 The characteristics of the dispersion are shown in Table 1, column 4.

TABLE 1

Characteristics of the dispersions from Examples 1 to 4:

15	Example No.	1	2	3	4
	Solids content (% by weight)	43.2	41.9	40.3	38.4
	pH	9.4	9.5	9.5	9.3
20	LT value	56	49	61	76
	Isobutanol content (% by weight)	0.4	0.4	4.9	12.6
25	Viscosity (mPa.s)	42,000	pasty	900	4,000

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A continuous process for the preparation of an aqueous secondary polyacrylate dispersion having a long shelf life and based on a polyacrylate resin system by means of intensively dispersant screw extruders, wherein the preparation of the secondary dispersion is carried out, after the neutralization of the solvent-free copolymer melt or of the dissolved copolymer, in the shearing section of a screw extruder, and
5 the specific energy input is 0.001-0.25 kWh/kg, the residence time in the shear field is 0.1-120 sec, and the shear gradient is 1,000-12,000 1/sec.
2. A process as claimed in claim 1, wherein, before the dispersing step with water, acidic or basic groups of the copolymer melt are neutralized.
15
3. A process as claimed in claims 1 and 2, wherein the neutralization of the solvent-free copolymer melt is advantageously carried out in the mixing zone of the self-purging twin-screw extruder or in the shearing section of an intensively dispersing screw extruder, and
20 the specific energy input is 0.005-0.05 kWh/kg and the residence time in the mixing zone is 0.1-60 sec.
4. A process as claimed in any of claims 1 to 3, wherein the material system is self-emulsifying.
- 25 5. A process as claimed in any of claims 1 to 4, wherein the secondary dispersion is stabilized by the carboxylate groups present at the surface of the latex particles.
- 30 6. A process as claimed in any of claims 1 to 5, wherein the polyacrylate to be dispersed is a solution copolymer or preferably a mixture of two solution copolymers, only one of the two copolymers containing acid groups or base groups.